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Night-time radical chemistry during the NAMBLEX campaign

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Abstract

Night-time chemistry in the Marine Boundary Layer has been modelled using a number of observationally constrained zero-dimensional box-models. The models were based upon the Master Chemical Mechanism (MCM) and the measurements were taken during the North Atlantic Marine Boundary Layer Experiment (NAMBLEX) campaign at Mace Head, Ireland in July–September 2002.

The model could reproduce, within the combined uncertainties, the measured concentration of HO_2 (within 30−40%) during the night 31 August–1 September and of HO_2+RO_2 (within 15−30%) during several nights of the campaign. The model always overestimated the NO_3 measurements made by Differential Optical Absorption Spectroscopy (DOAS) by up to an order of magnitude or more, but agreed with the NO_3 Cavity Ring-Down Spectroscopy (CRDS) measurements to within 30−50%. The most likely explanation of the discrepancy between the two instruments and the model is reaction of the nitrate radical with inhomogeneously distributed NO, which was measured at concentrations of up to 10 ppt, even though this is not enough to fully explain the difference between the DOAS measurements and the model.

A rate of production and destruction analysis showed that radicals were generated during the night mainly by the reaction of ozone with light alkenes. The cycling between HO_2/RO_2 and OH was maintained during the night by the low concentrations of NO and the overall radical concentration was limited by slow loss of peroxy radicals to form peroxides. A strong peak in $[NO_2]$ during the night 31 August–1 September allowed an insight into the radical fluxes and the connections between the HO_x and the NO_3 cycles.

1 Introduction

Radical chemistry during the night is controlled by the reactivity of ozone and of the nitrate radical. NO_3 is formed by the reaction of ozone and nitrogen dioxide (R1), but is present in significant concentrations only during the night, since it is quickly photolyzed by sunlight yielding either NO_2 or NO.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{R1}$$

NO_3 reacts with NO_2 to form N_2O_5, which thermally decomposes giving back NO_2 and NO_3 (R2). In the night-time boundary layer NO_3 and N_2O_5 quickly reach an equilibrium, unless the concentration of NO_2 is very low (Allan et al., 2000). N_2O_5 therefore acts as an important reservoir of oxidized nitrogen, directly or through the production of HNO_3 via the reaction with water (R3–R4) (Atkinson et al., 2003). N_2O_5 and NO_3 are also uptaken on aerosol.

$$NO_3 + NO_2 + M \rightleftharpoons N_2O_5 + M \tag{R2}$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{R3}$$

$$N_2O_5 + 2H_2O \rightarrow 2HNO_3 + H_2O \tag{R4}$$

NO_3 reacts with alkenes and some aromatics (Atkinson and Arey, 2003). The reaction proceeds either by H-abstraction or by addition to the double-bond producing peroxy and nitro-peroxy radicals which then react with NO, HO_2 or other peroxy radicals. Reaction with NO leads to the formation of HO_2 and, via the reaction of HO_2 with NO and/or O_3, to the formation of OH. In this way the nitrate radical acts as a source of HO_x during the night, when ozone and formaldehyde photolysis, the main sources of HO_x radicals during the day, are absent.

Another significant source of HO_x during the night is the decomposition of Criegee intermediates from the reaction of ozone with alkenes (Atkinson and Arey, 2003). The relative importance of NO_3 and O_3 as HO_x sources during the night depends on NO_x and hydrocarbon concentrations.

Many studies on NO_3 chemistry have been reported, e.g. Allan et al. (1999, 2000); Brown et al. (2003, 2004); Vrekoussis et al. (2004), but comparatively few have been published on HO_x night-time chemistry, expecially in the marine boundary layer. HO_2

was measured at night at concentrations of up to 7.6×10^{7} molecule cm^{-3} at Oki Island (Kanaya et al., 1999), 1.4×10^{8} molecule cm^{-3} at Okinawa (Kanaya et al., 2001) and 1.1×10^{8} molecule cm^{-3} at Rishiri Island (Kanaya et al., 2002). In all three campaigns the radical source was attributed to the reactions of alkenes and monoterpenes with O_3 with little or no contribution by NO_3 chemistry. Carslaw et al. (1997) found a positive correlation between NO_3 and HO_2+RO_2 during spring and autumn at Weybourne on the North Sea, evidence of production of peroxy radicals from reactions of the nitrate radical. No OH and HO_2 measurements were made during that campaign. Salisbury et al. (2001) reported a study of nocturnal peroxy radicals at Mace Head under comparatively clean conditions during the EASE97 campaign. HO_2 was measured on two nights at concentrations of up to 5.1×10^{7} molecule cm^{-3}. Their study showed that ozone-initiated oxidation routes of alkenes outweighed those of NO_3, except when the air was coming from the west and south-west sector. An analysis of peroxy radicals during the night at Cape Grim was also reported by Monks et al. (1996).

This paper discusses modelling and measurements of radicals (OH, HO_2, organic peroxy radicals and NO_3) at Mace Head, Ireland, during the North Atlantic Marine Boundary Layer Experiment (NAMBLEX) (Heard et al., 2005). The campaign took place during the summer of 2002 (July–September) and involved ten British universities (Aberystwyth, Bristol, Birmingham, Cambridge, East Anglia, Edinburgh, Leeds, Leicester, UMIST, York) and the National University of Ireland, Galway. A complete overview of the campaign is in Heard et al. (2005). Description and analysis of the radical measurements can be found in Smith et al. (2006) and Saiz-Lopez et al. (2005). Two companion papers describe OH and HO_2 day-time chemistry (Sommariva et al., 2006) and peroxy radical (HO_2 and HO_2+RO_2) chemistry (Fleming et al., 2005) during NAMBLEX.

Section 2 of the paper briefly describes the models and the measurements used in this work. Sections 3 and 4 discuss the model-measurements comparisons of OH, HO_2, HO_2+RO_2 and of NO_3, NO_3+N_2O_5, respectively. Section 5 contains a detailed rate of production and destruction analysis and Sect. 6 an analysis of one particular night of NAMBLEX (31 August–1 September). Finally, Sect. 7 contains the summary and the main conclusions of this work.

2 Models and measurements

The models used in this work are described in detail in Sommariva et al. (2006). They were built following the guidelines detailed in Carslaw et al. (1999) and in Sommariva et al. (2004) and using version 3.1 of the Master Chemical Mechanism (MCM, http://mcm.leeds.ac.uk/).

Four base models, with different degrees of chemical complexity, were used to study the impact of hydrocarbons, oxygenates and peroxides on the calculated concentrations of radicals. All the models were constrained to 15 min averages of measured concentrations of CO, CH_4, H_2, O_3, NO, NO_2, HCHO, selected NMHCs, H_2O and to measured temperature and photolysis rates ($j(O^1D)$, $j(NO_2)$, j(HONO), both channels of j(HCHO), $j(CH_3COCH_3)$, $j(CH_3CHO)$). The constraints of the different models used in this work are shown in Table 1.

The NMHCs data were linearly interpolated to 15 min. The measured species were: ethane, propane, i-butane, n-butane, i-pentane, n-pentane, n-hexane, n-heptane, ethene, propene, acetylene, trans-2-butene, but-1-ene, i-butene, cis-2-butene, 1,3-butadiene, isoprene, benzene, toluene, ethylbenzene, m-xylene + p-xylene, o-xylene plus three oxygenates (acetaldehyde, methanol, acetone) and two peroxides (H_2O_2 and CH_3OOH) (Lewis et al., 2005). SO_2 was not measured and was set to a constant value of 55 ppt (Berresheim et al., 2002).

No peroxides measurements were available after 30 August. Even before 30 August their concentrations, and in particular [CH_3OOH], were often below or close to the detection limit (0.02 ppb, Morgan and Jackson (2002)). HCHO was measured with two techniques (Still et al., 2005). The University of East Anglia (UEA) measurements were used to constrain the model, because they were made closer to the radical measurements than the Leeds measurements. HCHO data were not available after August

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21, therefore the models for the following days were not constrained to HCHO, which was instead calculated. Also, measurements of chloroform ($CHCl_3$) were not available before 3 August. The omission of peroxides, formaldehyde and chloroform did not influence significantly the calculated concentrations of radicals at night. In the models which were not constrained to the concentrations of oxygenates and hydroperoxides concentrations ("clean" and "full" models), these species were calculated as intermediates and the calculated concentrations were, especially for species with longer lifetimes, more than an order of magnitude less than the measured concentrations, because of the importance of transport.

Dry deposition terms were also included using the values of Derwent et al. (1996) except for peroxides (1.1 cm s^{-1} for H_2O_2 and 0.55 cm s^{-1} for organic peroxides), methyl and ethyl nitrate (1.1 cm s^{-1}) and HCHO (0.33 cm s^{-1}) (Brasseur et al., 1998). Dry deposition velocity for CH_3CHO and other aldehydes was assumed to be the same as that for HCHO. A clear diurnal cycle of the boundary layer (BL) was not always recognizable during NAMBLEX and often the synoptic pattern dominated over the local conditions (Norton et al., 2006). On many days during the campaign the boundary layer was roughly constant throughout the day with heights of 700–1500 m, while on a few days, such as 9 August, the BL showed a diurnal variation with a height of 1000–1500 m during the day and 400–500 m during the night.

Heterogeneous uptake was calculated using Eq. (1) assuming irreversible loss of gas-phase species on aerosol.

$$k_{het} = \frac{A\bar{v}\gamma}{4} \tag{1}$$

where A is the total aerosol surface area, $\bar{v}$ is the mean molecular speed and γ is the temperature dependent gas/surface reaction probability. The values of γ used for HO_2, NO_3, N_2O_5 were 0.006 (at 298 K), 0.004 and 0.032, respectively (Gratpanche et al., 1996; Allan et al., 1999; Behnke et al., 1997).

The models were used to calculate OH, HO_2, total peroxy radicals (HO_2+RO_2), NO_3 (or NO_3+N_2O_5) for several nights of the campaign. The model results were compared

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to the measurements. OH and HO_2 were measured by laser-induced fluorescence (LIF) using the FAGE (Fluorescence Assay by Gas Expansion) technique. During the night the detection limits for the two radicals were 6×10^4 and 1×10^6 molecule cm^{-3}, respectively (Smith et al., 2006). Total peroxy radicals (HO_2+RO_2) were measured by the PERCA (Peroxy Radical Chemical Amplifier) technique with a detection limit of about 0.5 ppt. The FAGE and the PERCA instruments are described in Smith et al. (2006) and Fleming et al. (2005), respectively.

NO_3 was measured by Differential Optical Absorption Spectroscopy (DOAS). The DOAS instrument was located about 100 m from the shore with the retro-reflector on an island about 4 km west of Mace Head. The total light path was 8.4 km and NO_3 was measured in the 645–680 nm spectral region with a detection limit of 0.4–0.5 ppt (Saiz-Lopez et al., 2005). A Cavity Ring-Down Spectrometer (CRDS) was also present at Mace Head. It was located about 25 m inland from the DOAS. The CRDS measured NO_3 and NO_3+N_2O_5 in the spectral region 655–675 nm with an estimated light path of ~20 km and a detection limit of approximately 1 ppt, depending on the aerosol loading (Bitter et al., 2005). The details of the two instruments are given in Saiz-Lopez et al. (2005); Bitter et al. (2005).

The modelling of the night-time chemistry in the marine boundary layer was concentrated on a few nights, which can be divided roughly in two periods. The semi-polluted period at the beginning of August (1–5 August), and the unpolluted period during the rest of the campaign (Heard et al., 2005). The semi-polluted period was characterized by comparatively high concentrations of NO_x, CO, and NMHCs (Table 2). Acetylene, an anthropogenic marker, was 2 to 3 times higher than during other periods of the campaign. The five-day back trajectories showed that the air masses arriving at Mace Head were coming from east-northeast, passing over Northern England and Ireland (Norton et al., 2006). Most of the rest of the campaign and particularly the night 31 August–1 September was characterized by comparatively unpolluted conditions, with low NO_x and hydrocarbons concentrations (Table 2) and air masses of oceanic origin coming from west, north-west and south-west. More details on the chemical conditions during NAMBLEX can be found in Heard et al. (2005) and a complete discussion of the meteorology during the campaign can be found in Norton et al. (2006).

3 OH, HO_2 and RO_2

OH and HO_2 were measured during one night (31 August–1 September). OH was always below the instrumental detection limit (6×10^4 molecule cm^{-3}). Late evening and early morning measurements showed concentrations of the order of 1–2×10^5 molecule cm^{-3}, about twice as much as the modelled concentration during the night (Fig. 1(a)). The model overestimated the measurements at sunset, but underestimated them at sunrise suggesting the presence of an OH source unaccounted for or underestimated by the model, such as HONO (Smith et al., 2006).

HO_2 concentrations of the order of 1–3×10^7 molecule cm^{-3} were detected, similar to previous measurements in Mace Head during two nights of the EASE97 campaign (1.5–5×10^7 molecule cm^{-3}, Salisbury et al. (2001)). The models overestimated HO_2 by about 30–40% (Fig. 1(a)). Compared to daytime, when the model overestimated the measurements by about a factor of 2 (Sommariva et al., 2006), the agreement between the model and the measurements is reasonably good and well within the combined uncertainties of the model and of the instrument (25–30% and 50%, respectively, Sommariva et al., 2004).

PERCA measurements were taken every night during the campaign. The comparisons with the model results are shown in Fig. 1(b) and Fig. 2(a). The agreement between modelled and measured HO_2+RO_2 was within 15–30% during most of the modelled nights. Contrary to the day-time, the model showed a tendency to underestimate the PERCA measurements during the night (see Fig. 4b in Fleming et al., 2005). During the night 20–21 August the model underestimated the measurements by about 50% (Figs. 1(b)–2(a)). On some occasions measured [HO_2+RO_2] increased throughout the night, which appeared to be related to NO_x events, but was not always reproduced by the model (e.g. 17–18 August). Fleming et al. (2005) showed that the

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measured peroxy radicals concentration during the night was generally higher at higher $[NO_x]$.

The speciation of modelled peroxy radicals during NAMBLEX, showed that CH_3O_2 was the dominant radical during the night. In the unpolluted period CH_3O_2 was up to 60% of HO_2+RO_2, while HO_2 was about 20% of HO_2+RO_2. This was approximately the reverse of the day-time proportion and in good agreement with the results of the EASE97 campaign by Salisbury et al. (2001). During the semi-polluted period CH_3O_2 was up to 40% of HO_2+RO_2, while HO_2 was about 40% of HO_2+RO_2 indicating a faster production of inorganic radicals in presence of higher NO_x and NMHCs concentrations. The modelled HO_2/(HO_2+RO_2) ratio was about 50% higher than the measured ratio, as a consequence of the overestimation of HO_2 (Fleming et al., 2005).

Comparing the results of the different models (Table 1) it is clear that the difference between the "full", 'fulloxy' and "fulloxyper" models was negligible (Figs. 1 and 2(a)), indicating that additional constraints of oxygenates and peroxides did not influence significantly the concentrations of HO_2 and RO_2. However for the "clean" model, which was constrained only to CO and CH_4, calculated concentrations of HO_2 (Fig. 1(a)) and HO_2+RO_2 (Figs. 1(a) and 2(a)) were about an order of magnitude lower than the concentrations calculated by the "full" and "fulloxy" models. This was due to the fact that the only peroxy radical of the "clean" model was CH_3O_2, which mainly came from CH_4 oxidation, a very slow reaction at night ($k_{CH_4+NO_3}<1\times10^{-18}$ cm^3 molecule^{-1} s^{-1}, Atkinson et al., 2003).

Similar results were obtained during the baseline periods of the SOAPEX-2 campaign in the Southern Hemisphere using a model similar to the "clean" model (Sommariva et al., 2004). On one occasion (15–16 February 1999), late evening and early morning measurements of OH and HO_2 were made, showing late evening concentrations of HO_2 about a factor of two larger than the predictions of the "clean" model (Fig. 2(b)). The model underestimated HO_2+RO_2 by about almost an order of magnitude, a similar factor to that found when using the 'clean' model for NAMBLEX (Fig. 1(b)). Since the more detailed models ("full", "fulloxy" and "fulloxyper") provide much better agreement with the NAMBLEX observations of HO_2+RO_2, this observation suggests that even in the extremely clean conditions of Cape Grim (Sommariva et al., 2004) CO and CH_4 alone cannot account for the radical budget and even low concentrations of NMHCs play a significant role.

4 NO_3

The nitrate radical was measured for many nights during NAMBLEX by DOAS and CRDS (Saiz-Lopez et al., 2005; Bitter et al., 2006[1]). Data from the CRDS instrument were available only for the initial semi-polluted period of the campaign when the concentrations were higher (Table 2). The model-measurements comparisons are shown in Fig. 3.

The models always underestimated the DOAS measurements of $[NO_3]$, on average by about a factor of 4–5 up to a factor of 10 (Figs. 3(b)–3(c)). On some nights, like 18–19 and 19–20 August, the modelled concentrations of NO_3 were up to 60 times lower than the DOAS measurements. This was similar to the results obtained for the one night in the SOAPEX-2 campaign which was modelled (15–16 February 1999) and for which NO_3 measurements were available (Fig. 2(b)).

The agreement between modelled NO_3 and $NO_3+N_2O_5$ and the measurements by CRDS was generally better (Fig. 3(a)). Modelled concentrations were typically within 30–50% of the measurements, with the model showing a tendency to underestimate the measurements. Note that on the night 1–2 August the high CRDS measurements before midnight (Fig. 3(a)) were subject to a larger uncertainty than the measurements taken later in the night, due to the higher aerosol optical depth (Bitter et al., 2006[1]).

A detailed comparison between the DOAS and CRDS measurements and a discussion of the possible reasons for the different $[NO_3]$ measured by the two instruments

[1]Bitter, M., Ball, S. M., Povey, I. M., Jones, R. L., Saiz-Lopez, A., and Plane, J. M. C.: Measurements of NO_3, N_2O_5, OIO, I_2, water vapour and aerosol optical depth by broadband cavity ringdown spectroscopy during the NAMBLEX campaign, in preparation, 2006.

is presented in Bitter et al. (2006)[1]. An important point to note is that while the DOAS measurements were averages over a long path (8.4 km at Mace Head) crossing a branch of sea, the CRDS measurements were point measurements made about 100 m from the shore (Heard et al., 2005). The fact that the model-DOAS discrepancy was similar in such diverse conditions as SOAPEX-2 (Sommariva et al., 2004) and NAMBLEX (Table 2) in contrast with the good agreement between the model and the CRDS point measurements suggests that the zero-dimensional approach used in this work might not be suitable to model DOAS measurements.

Under the relatively low [NO_2] conditions at Mace Head, NO_3 and N_2O_5 rapidly equilibrate (R3) and any loss of N_2O_5 resulted in the removal of NO_3 from the system. N_2O_5 can be removed by reaction with H_2O and by uptake on aerosol. Previous studies have shown that, under certain conditions (semi-polluted air masses with little marine influence), removal of N_2O_5 can be a major loss pathway for NO_3 (Allan et al., 1999, 2000). Semi-polluted conditions were experienced at the beginning of the NAMBLEX campaign (1–2 August). To test the impact of N_2O_5 uptake on modelled [NO_3] the model was run with an uptake rate coefficient for N_2O_5 equal to 0.016 (in the base model $\gamma_{N_2O_5}$=0.032). The effect on modelled [NO_3] was negligible (model "fulloxy-n2o5" in Fig. 3(a)), showing that the model was not very sensitive to N_2O_5 heterogeneous uptake under these conditions.

An important issue in night-time chemistry is the concentration of nitric oxide. NO rapidly reacts with radicals, for which there are few night-time sources, and with ozone. With 30 ppb of O_3, NO has a lifetime of about 1 min at 283 K. Its concentration is therefore expected to be extremely low during the night. However, this is not always the case, since NO local sources might be present. During NAMBLEX, NO concentrations above the detection limit of the instrument (3–4 ppt) were often detected during the night. The night-time average mixing ratio was about 15–20 ppt during the semi-polluted period and about 6.5–7 ppt during the unpolluted period. This suggests the presence of a local source of NO, possibly emissions from the soil during the night.

The emission of NO from soils might provide an important NO_3 sink (via the NO+NO_3

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reaction), particularly in Ireland, because of the presence of peaty soils around Mace Head (Williams and Fehsenfeld, 1991; Williams et al., 1992; Regina et al., 19998). Since the DOAS sampled over the sea, while the CRDS sampled over the land, local NO soil emissions might explain the difference between the two instrument's measurements and the underestimation of the DOAS observations by the model. This hypothesis is discussed in more detail in Bitter et al. (2006)[1], who used a simple box model to show how NO emitted over land could suppress NO_3 at the levels observed by CRDS but, as the air mass was advected over the sea and away from the NO source by off-shore winds, the concentration of NO_3 would steadily increase to the levels observed by DOAS. Conversely under a sea-breeze, the higher NO_3 concentrations maintained over the sea are rapidly titrated by the NO emissions at the shore when the air mass arrives over the land (Bitter et al., 2006)[1].

The "clean" and the "fulloxy" models were therefore run with measured NO during the day and [NO]=0 during the night to understand the impact of nitric oxide on modelled NO_3 and to see if this could explain the discrepancy between the model and the DOAS measurements. The results of these test runs are shown in Fig. 4. Also shown are the results of model runs with [DMS]=0 and with both [NO] and [DMS]=0.

Figure 4 suggests that setting [DMS] to zero did not have a significant effect on the calculated NO_3, except when the models were also constrained to zero [NO]. In fact, when the models were constrained to measured NO, the main fate of NO_3 was the reaction with NO. The models showed that when both [DMS] and [NO] were set to zero, NO_3 mainly reacted with NMHCs. These reactions were slower, resulting in a higher [NO_3] and the models became more sensitive to DMS. Therefore, when both [DMS] and [NO] were set to zero, [NO_3] became 3–4 times larger than when NO was present. However, this was not enough to increase the calculated [NO_3] up to the values measured by the DOAS and caused an overestimation of the CRDS measurements (about 40–50% and up to a factor of 3).

Another issue which might be significant in explaining the differences between the DOAS, the CRDS and the models is the vertical profile of NO_3. Saiz-Lopez et al. (2005)

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observed a positive vertical NO_3 gradient over Mace Head, which they attributed in part to the temperature and NO_2 vertical profile and in part to the reaction of NO_3 with DMS, whose concentration was higher near the sea surface (Purvis et al., 2005). The NO_3 gradient could also cause a downward motion of NO_3 over the ocean. This could in part explain the fact that the DOAS measurements were higher than the CRDS measurements (Bitter et al., 2006)[1]. In fact, while the heights of the CRDS and of the DOAS telescope were roughly the same, the DOAS retro-reflector was located at a higher position, so the average height of measurement for DOAS measurements was greater than that of the CDRS. A significant vertical gradient in $[NO_3]$ would compromise the zero-dimensional model used in this study and lead to poor prediction of the measured $[NO_3]$.

5 Analysis of the radical fluxes

The rates of production and destruction of modelled OH, HO_2 and NO_3 were calculated for the nights 1 and 2 August, characterized by semi-polluted conditions and higher $[NO_3]$, and 31 August and 1 September, characterized by unpolluted conditions and lower $[NO_3]$ (Table 2). The objective of the analysis was to identify the most important reactions and the processes driving the night-time chemistry under those conditions. The "fulloxy" model was used as reference. The results of the rate of production and destruction analysis are shown in Fig. 5 for HO_x during the night 31 August–1 September and in Fig. 6 for NO_3 during the nights of 1–2 August and 31 August–1 September.

There were essentially two interacting chain cycles, one directly linking OH to HO_2 via CO, the other proceeding via RO_2, with CH_3O_2 as the main immediate precursor of HO_2. The time constant of the former was quite short, of the order of 1 s, and was largely determined by the OH reactions shown in Fig. 5(a), primarily involving CO, but also HCHO, O_3 and H_2. The route through CH_3O_2 involved not only reaction of OH with CH_4, but also with NMHCs. There were also two other, longer time constants associated with the chain cycle, involving the conversion of CH_3O_2 to HO_2 by reaction

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with NO and of HO_2 to OH by reaction with O_3 and NO, with the latter decreasing in importance with time. If there was no source term, the coupled radical pool would slowly decay, via both peroxy-peroxy and $OH+NO_2$ reactions. There was, however, a radical source (mainly of OH and CH_3O_2), provided by Criegee intermediates formed from O_3+alkene reactions (mainly propene, c-2-butene, t-2-butene, c-2-pentene, t-2-pentene), that helped to maintain the radical concentrations, although there was generally a slow decrease with time. The decomposition of CH_3SO_3 to give SO_3 and CH_3O_2 and the reaction of CH_3CO_3 with NO provided additional CH_3O_2 sources.

Fleming et al. (2005) calculated the fluxes of radicals from alkenes+O_3 and alkenes+NO_3 during several nights of the NAMBLEX campaign. They showed that ozone reactivity dominated the formation of radicals most of the nights, except when the NO_3 concentration was high, such as in the semi-polluted period at the beginning of the campaign. This is in broad agreement with the results of the reaction rate analysis discussed above (it must be noted that Fleming et al. (2005) used [NO_3] as measured by DOAS, which was typically an order of magnitude higher than the modelled [NO_3] used here).

On the night of 1-2 August, the main formation and destruction routes for NO_3 were NO_2+O_3 and NO_3+NO_2 respectively (Fig. 6). The $NO_3+NO_2 \rightleftharpoons N_2O_5$ equilibration was rapid but led to a net sink for NO_3, because of the loss of N_2O_5 by hydrolysis and heterogeneous uptake. On 31 August–1 September, the N_2O_5 loss was less significant than on 1–2 August, so that the forward and reverse steps in the equilibration balanced. The main losses of NO_3 on both nights were the reactions with NO and with DMS. On the unpolluted night 31 August–1 September the two reaction rates were comparable ($\sim 5\times10^3$ molecule cm^{-3} s^{-1}), while on the semi-polluted night 1–2 August the reaction with NO was about a factor of 4 faster (Fig. 6). In fact, on this night the concentration of NO was generally higher (about a factor of 3 during the night), as polluted air arrived at Mace Head from the north-east, and the DMS concentration was lower. Other sinks for NO_3 were the reactions with a range of NMHCs (mainly alkenes like but-1-ene and t-2-butene and aromatics like phenol and cathecols) and peroxy radicals (HO_2 and

CH_3O_2).

6 A case-study night

Measurements of HO_2, HO_2+RO_2 and NO_3 were all made on the night between 31 August and 1 September. OH was also measured, but was always below the detection limit. A large spike of NO_2 occurred in the middle of the night allowing the couplings between the species and the cycles of HO_x and NO_3 to be studied.

Between 22:00 and 24:00 on 31 August the measured concentration of NO_2 rose from its "normal" value of 40 ppt to about 300 ppt. The concentration of NO did not change as much (Fig. 7). The spike appeared to be related to a change in the local wind direction from ~200°(S-SW, from the open sea) to ~150°(S-SE, along the coastline). The most probable explanation was a local source of NO_2, which was brought to the instrument as the wind shifted direction. Figure 8 shows the reactions of the most important species in the night-time chemistry on 31 August–1 September (Sect. 5) and their connections via ozone and NO. O_3 in particular had a double role. It converted HO_2 to OH, and also reacted with NO_2 to generate NO_3. NO_2 was produced from NO, through its reactions with CH_3O_2 and HO_2. NO_3 and NO_2 were linked through the reaction NO_3+NO and through the equilibrium of N_2O_5. Ozone, nitrogen oxides (NO, NO_2, NO_3) and OH, HO_2 and CH_3O_2 were therefore interconnected and a change in the concentration of one of these species, namely NO_2, quickly propagated through the cycles to affect all the others.

The fluxes during the NO_2 event (23:00) and under "normal" conditions (24:00) are shown in Fig. 8. It can be seen that with high [NO_2] the rate of O_3+NO_2 was about 6 times faster than with low [NO_2]. This caused an increment in [NO_3] and the rapid consumption of ozone. With higher NO_3 concentration the rates of the reactions with DMS and NO (to regenerate NO_2) increased by a factor of 8 and 3, respectively. The consequence was a decrease in ozone by about 30% and of NO by almost a factor of 4, which is clearly visible in the measurements (Fig. 7). With less O_3 and NO present, the conversion between HO_2 and OH slowed down to about half its normal rate. While OH continued to be produced by the decomposition of the Criegee intermediates (mainly CH_3CHOO), the decrease in the propagation rates lead to a decrease in [OH].

The measurements reflected these changes. In correspondence to the NO_2 spike the concentration of NO and O_3 decreased (Fig. 7) and the concentration of NO_3 showed a slight increase (Fig. 3(c)). The DMS profile showed an initial increase until 22:30, which was then followed by a fast decline until midnight, due to the reaction with NO_3 (Fig. 7).

7 Conclusions

Night-time measurements of radicals were made during a field campaign (NAMBLEX) in a marine environment in the Northern Hemisphere. OH was always below the detection limit (6×10^4 molecule cm^{-3}), but HO_2 concentrations of 1–3×10^7 molecule cm^{-3} were measured during one night (31 August–1 September). HO_2+RO_2 and NO_3 were measured on several nights. On the night of 31 August–1 September simultaneous measurements of HO_2, HO_2+RO_2 and NO_3 were available, together with many other supporting measurements, allowing a thorough study of night-time chemistry. The radicals concentrations were calculated using a set of zero-dimensional box-models, based on the Master Chemical Mechanism and constrained to measured species and parameters.

The agreement between the model and the measurements was reasonably good for HO_2, with a tendency to overestimate the measurements by less than 40%. The agreement with HO_2+RO_2 was more variable, but within 15–30% during most of the nights. A model containing only CO and CH_4 chemistry always underestimated both [HO_2] and [HO_2+RO_2] by about an order of magnitude, showing that most of the peroxy radicals generated during the night derived from the oxidation of NMHCs. The most important peroxy radicals were HO_2 (20% on unpolluted nights and 40% on semi-polluted nights) and CH_3O_2 (60% on unpolluted nights and 40% on semi-polluted nights).

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The measurements indicated that the radical concentrations remained more or less constant throughout the night, suggesting a nocturnal radical source. The model showed that reaction of O_3 with alkenes (mainly propene, butenes and pentenes) was a slow but steady source of OH during the night which compensated the slow removal of radicals via the formation of peroxides from peroxy-peroxy reactions.

The model consistently underestimated [NO_3] measured by DOAS by a factor of 5–10 or more. The agreement with the CRDS measurements during NAMBLEX was much better, within 30–50%. Scavenging of NO_3 by NO over land was explored as one of the possible explanations for the discrepancy between the two instruments and with the model. Reaction with NO was the main loss process for NO_3 during the night 31 August–1 September, followed by the reaction with DMS. When the model was run with [NO]=0, NO_3 mainly reacted with DMS resulting in an increase in modelled NO_3 of about 50%. With [DMS]=0, modelled NO_3 increased by about 70–80% and the main losses for the nitrate radical became the reactions with a variety of alkenes, aromatics and peroxy radicals or the uptake on aerosol. The only source of NO_3 was the reaction of NO_2 with O_3.

On 31 August–1 September a spike of NO_2 of up to 300 ppt allowed an examination of the coupling between NO_3 and HO_x. The increase in NO_2 caused an acceleration of the reaction with O_3, increasing the production of NO_3 (and hence the rates of its reactions with DMS and NO) and depleting O_3. The decrease in NO and O_3 caused a slowing of the $HO_2 \rightarrow OH$ conversion rate.

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Table 1. Models used in this work.

Base Models	Constraints
"clean"	H_2, O_3, NO, NO_2, HCHO and H_2O, temperature, photolysis rates. CO, CH_4
"full"	as "clean" + 22 hydrocarbons, DMS, $CHCl_3$
"fulloxy"	as "full" + 3 oxygenates
"fulloxyper"	as "fulloxy" + 2 peroxides

Test Models	Constraints
"fulloxy-n2o5"	as "fulloxy" with $\gamma_{N_2O_5}$ = 0.016
"fulloxy-no"	as "fulloxy" with [NO] = 0
"fulloxy-dms"	as "fulloxy" with [DMS] = 0
"fulloxy-dms-no"	as "fulloxy" with [NO] and [DMS] = 0

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Table 2. Average (20:00–05:00) measurements on some selected nights during NAMBLEX. Concentrations in molecule cm^{-3}, temperature in °C.

Measurements	1–2 Aug	18–19 Aug	19–20 Aug	20–21 Aug	31 Aug–1 Sep
O_3	7.8×10^{11}	7.0×10^{11}	6.1×10^{11}	5.8×10^{11}	8.8×10^{11}
NO	3.2×10^{8}	1.5×10^{8}	2.0×10^{8}	1.3×10^{8}	9.2×10^{7}
NO_2	7.1×10^{9}	1.8×10^{9}	3.2×10^{9}	6.1×10^{9}	1.6×10^{9}
CH_4	5.0×10^{13}	4.7×10^{13}	4.8×10^{13}	4.7×10^{13}	4.6×10^{13}
CO	4.0×10^{12}	2.2×10^{12}	2.0×10^{12}	2.0×10^{12}	3.0×10^{12}
H_2	1.4×10^{13}	1.3×10^{13}	1.3×10^{13}	1.3×10^{13}	1.3×10^{13}
HCHO (UEA)	1.7×10^{10}	3.1×10^{9}	3.5×10^{9}	5.6×10^{9}	–
HCHO (Leeds)	3.9×10^{10}	1.5×10^{10}	1.4×10^{10}	1.8×10^{10}	–
Propene	6.0×10^{8}	3.6×10^{8}	5.3×10^{8}	5.8×10^{8}	2.5×10^{8}
DMS	6.4×10^{8}	2.6×10^{9}	1.0×10^{9}	1.1×10^{9}	1.1×10^{9}
Acetylene	7.2×10^{9}	1.5×10^{9}	1.9×10^{9}	1.5×10^{9}	3.5×10^{9}
Acetaldehyde	2.3×10^{10}	1.2×10^{10}	1.1×10^{10}	9.9×10^{9}	6.5×10^{9}
Temperature	17.5	13.8	12.8	14.3	14.1

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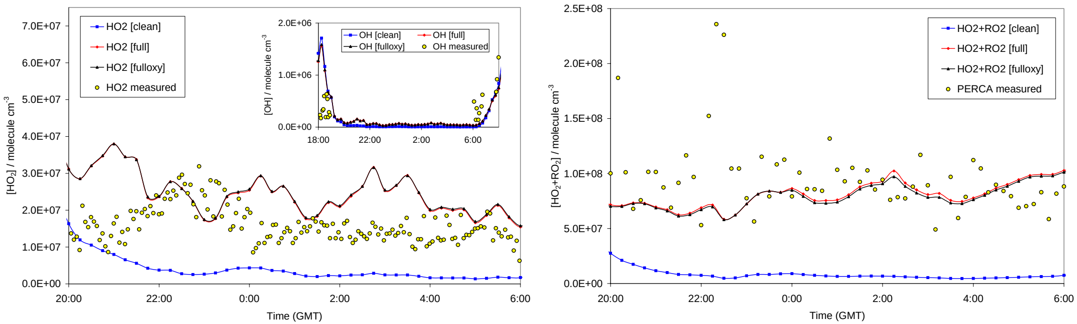

(a) (b)

Fig. 1. Model-measurement comparison for OH, HO_2 **(a)** and HO_2+RO_2 **(b)** during the night 31 August–1 September.

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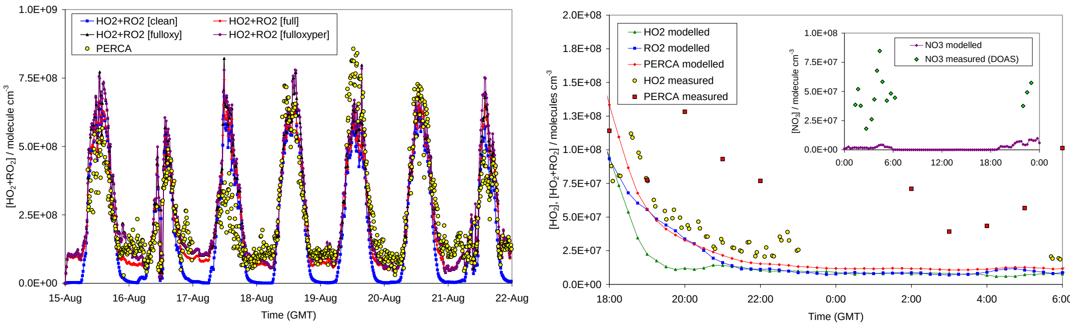

(a) (b)

Fig. 2. Model-measurement comparison for HO_2 and HO_2+RO_2 during the period 15–21 August of NAMBLEX **(a)**. Model-measurement comparison for NO_3, HO_2 and HO_2+RO_2 during the night 15–16 February 1999 of SOAPEX-2 **(b)**. The equivalent of the "clean" model was used for the SOAPEX-2 campaign (Sommariva et al., 2004).

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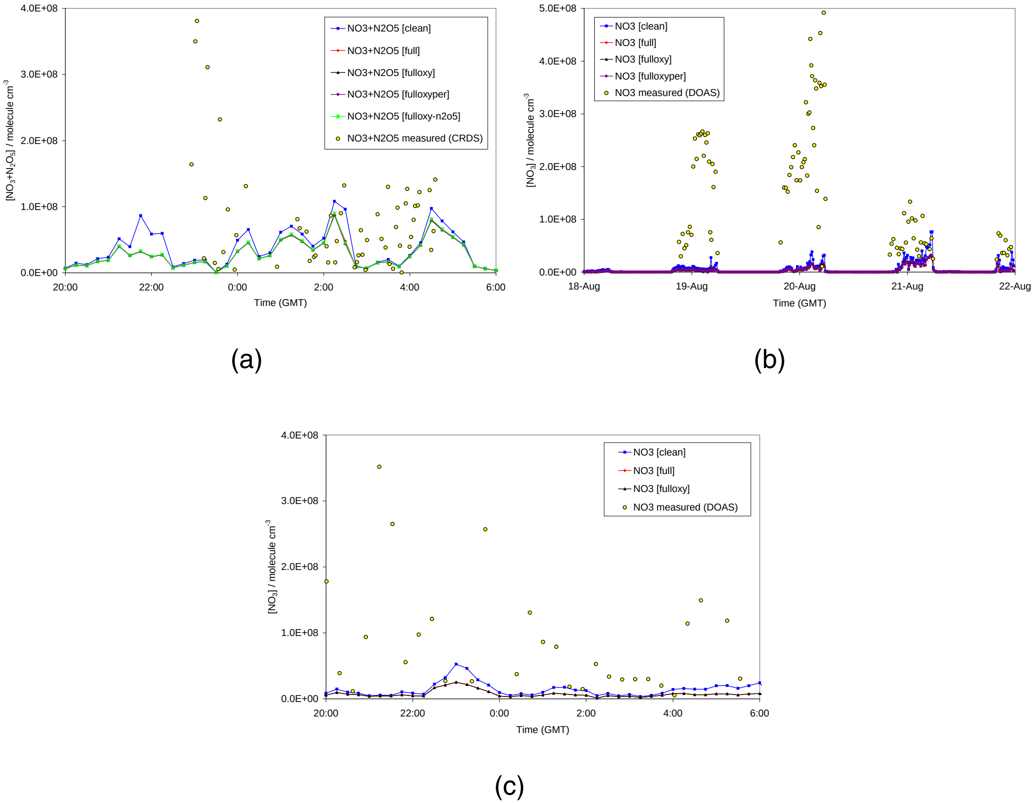

Fig. 3. Model-measurement for NO_3+N_2O_5, also showing the impact of N_2O_5 uptake, during the night 1–2 August **(a)** and for NO_3 during the period 18-22 August **(b)** and the night 31 August–1 September **(c)**.

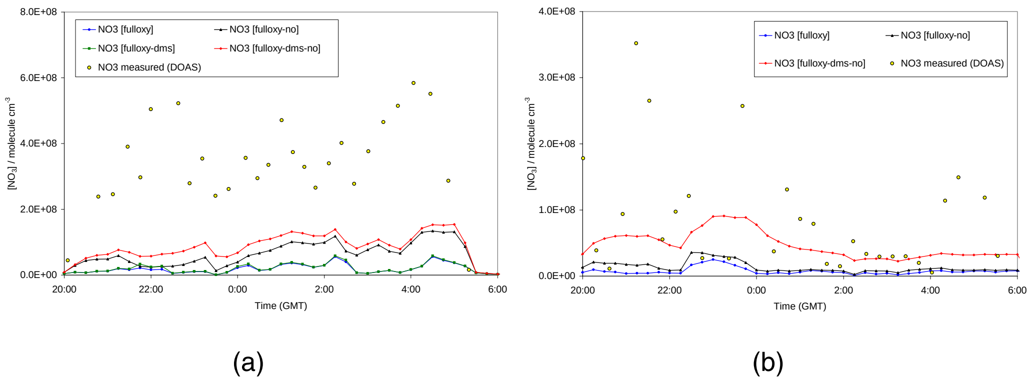

Fig. 4. Model-measurement comparison for NO_3 showing the impact of [NO]=0 and [DMS]=0 during the night 1–2 August **(a)** and 31 August–1 September **(b)**.

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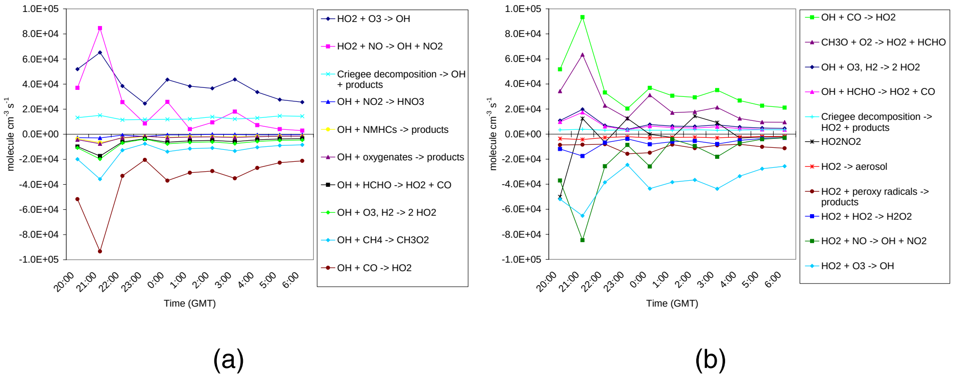

Fig. 5. Rates of production and destruction of OH **(a)** and HO_2 **(b)** during the night of 31 August–1 September.

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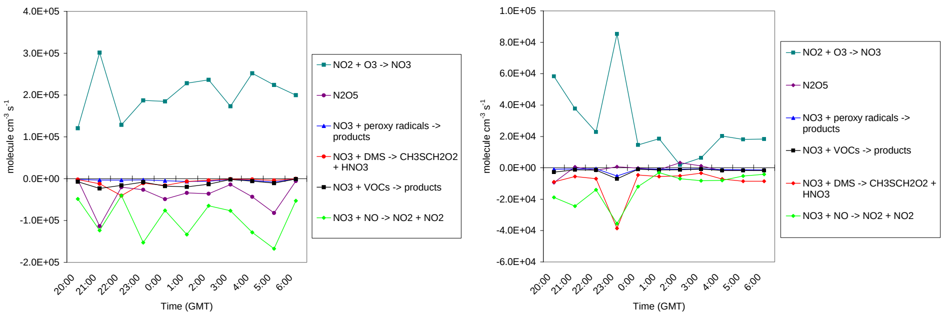

(a) (b)

Fig. 6. Rates of production and destruction of NO_3 during the night of 1–2 August **(a)** and during the night of 31 August–1 September **(b)**.

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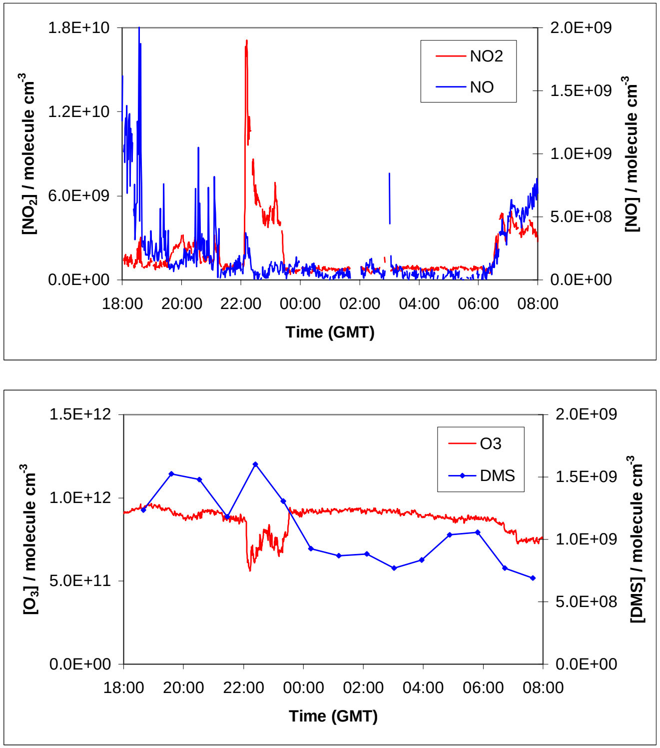

Fig. 7. O_3, DMS and NO_x concentrations measured during the night of 31 August–1 September.

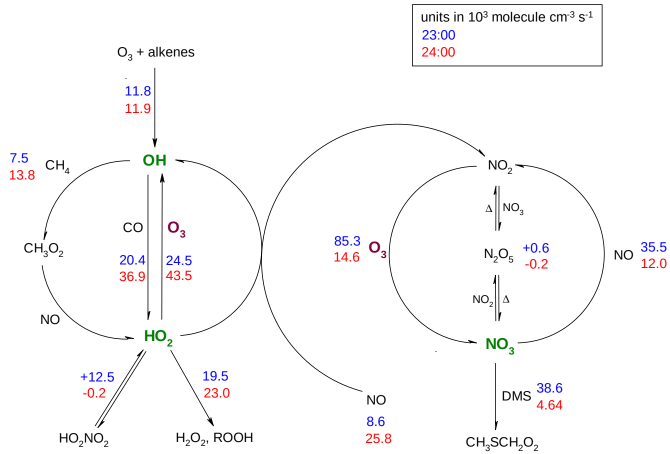

Fig. 8. Radical fluxes during the night of 31 August–1 September at 23:00 (in the middle of the NO_2 spike) and 24:00 (after the NO_2 spike).

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